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Michael F. Scalise

Name

Michael F. Scalise

Signature

October 3, 2003

Date of Signature

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Shah et al.

Serial No. : 09/872,110

Filed: : June 1, 2001

For : Ruthenium-Containing Ultrasonically
Coated Substrate For Use In A Capacitor
And Method Of Manufacture

Examiner : M. Cleveland

Group Art Unit : 1762

Assistant Commissioner for Patents
Alexandria, VA 22313-1450

DECLARATION UNDER 37 CFR 1.132

Sir:

Ashish Shah, one of the inventors in the above-referenced
patent application, states as follows:

1. Ashish Shah declares that he is one of the co-inventors of the subject matter of the above-referenced patent application and is an applicant named therein.

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2. That he earned a Bachelor of Science Degree in Electrical Engineering from Jadavpur University in Calcutta, India in 1985; earned a Masters of Science Degree in Electrical and Computer Engineering from the State University of New York at Buffalo in 1989; and earned a Ph.D. Degree in Electrical and Computer Engineering from the State University of New York at Buffalo in 1993.

3. That from September 1988 to June 1993 he worked at the New York State Institute of Superconductivity. While there, he was involved in the design, construction and optimization of thin and thick superconducting films, plasma vapor deposition systems, both in vacuum and at atmospheric pressure, processing of superconducting tapes on silver and by the powder-in-tube process, and film growth on single crystal, polycrystalline and metallic substrates. He also worked on thin film growth by excimer laser ablation and radio frequency powder synthesis.

4. That he has been employed at Wilson Greatbatch Technologies, Inc., the assignee of the present application, from 1995 to present where he has gained extensive work experience in capacitor technology, including capacitor package design, and fundamental research in implantable capacitor anodes and cathodes. He is currently a Senior Scientist at Wilson Greatbatch Technologies, Inc.

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5. That he believes the above educational training and work experience make him expertly qualified to opine with respect to matters related to the chemistry involved with the present invention.

6. That he has reviewed U.S. Patent Nos. 5,464,453 to Tong et al., 3,840,391 to Spitz et al., and 5,369,547 to Evans, all cited in the office action dated June 27, 2003, as relevant prior art to the present invention.

7. That he believes Tong et al. is cited for teaching a method of constructing capacitors. The capacitors include ruthenium contacted to a conductive substrate by several coating techniques including ultrasonic spray coating. Ruthenium oxide is preferred and is made from a precursor that is subsequently cured by pyrolytic methods. A preferred precursor is of a chloride alcohol solution that is cured at between ambient temperatures and 300°C to form a capacitor cathode component. Suitable alcohol-based solvents are of tert-butanol, isopropanol and ethanol while ruthenium trichloride is a preferred ruthenium oxide precursor.

8. That he believes Spitz et al. is cited for the teaching that an ultrasonic generator is useful for depositing a mist or aerosol of a solution on a heated substrate.

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9. That he believes Evans is cited for teaching an electrolytic capacitor including a porous coating of ruthenium coated on the inner surface of a metal container. In a preferred process, hydrated ruthenium chloride ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$) is dissolved in isopropyl alcohol. A tantalum or titanium substrate is then heated to about 85°C and the precursor solution spray contacted thereto. The substrate temperature results in rapid evaporation of the alcohol solvent leaving the ruthenium chloride behind. The substrate is then heated to about 300°C in air to convert the chloride and form the desired ruthenium oxide coating.

10. That he believes the combination of cited prior art patents does not teach that a ruthenium-containing oxide compound coated on a substrate by depositing a precursor thereof that is substantially devoid of a halide dissolved in a solution not containing an alcohol or a halide is beneficial for providing a pseudocapacitive component.

11. That he conducted comparative tests of ruthenium oxide derived from respective compounds according to the present invention and the prior art ultrasonically spray deposited on a heated substrate. The comparative tests were designed to follow the protocol of Example I set forth in the present application at page 19 to 20. This was done to prove that the use of a precursor of a ruthenium oxide-containing compound substantially devoid of a halide, such as chlorine, results in a significantly improved pseudocapacitive component in comparison to deposition of a ruthenium halide-containing compound.

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12. That the spray deposition tests consisted of aqueous solutions of either ruthenium nitrosyl nitrate ($\text{RuN}_3\text{O}_{16}$) or ruthenium chloride (RuCl_4) dissolved in about 100 cc. of de-ionized water. The former compound was in an amount of about 2.72 grams while the latter was in an amount of about 5.4 grams. About 0.5 cc. of nitric acid was added to the respective solutions. The solutions were stirred until the ruthenium-containing compounds were completely dissolved.

13. A gear pump was filled with the respective solutions and set to an injection flow rate of about 5 cc./min. A Sonotek ultrasonic aerosol generator was connected to the gear pump.

14. That a titanium foil substrate, about 0.005" thick, was cleaned and mounted on a temperature controlled substrate pedestal. The foil was heated to a temperature of about 220°C.

15. That the ultrasonic nozzle was positioned above the substrate at a height of about 8 cm. Power to the nozzle was set at 1.7 W. Dry and filtered air, at a flow rate of about 15 scft at about 3 psi, was used as a shroud gas.

16. That after the foil temperature stabilized, the syringe pump was turned on. This resulted in the respective ruthenium-containing solutions being pumped through the nozzle and atomized into tiny droplets deposited on the heated substrate. Upon contact with the substrate, at least some of the aqueous solvent was evaporated and at least some of the precursor was instantaneously converted to a ruthenium oxide coating.

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17. That both the ruthenium nitrosyl nitrate coated substrate and the ruthenium chloride solution coated substrate were removed from the heated pedestal and placed in a 400°C furnace for about 3 hours to ensure complete conversion of the respective precursors to the product ruthenium oxide coating.

18. That in the tests, the ruthenium nitrosyl nitrate precursor and the ruthenium chloride precursor were substantially completely converted to ruthenium oxide.

19. That the respective ruthenium oxide coated titanium foils were subjected to an Electron Spectroscopy Chemical Analysis (ESCA) to determine the atomic percent of residual chloride in the coating after decomposition of the respective precursors to the oxide. It is known that there is some minor percentage of chlorine in a ruthenium nitrate compound after the refining process. One of the reasons that ruthenium ores are refined is to remove latent chlorine.

20. That the results are set forth below in the table below.

Residual Chlorine
(Atomic Percent)

Precursor	Surface	20 Å	50 Å
RuN ₈ O ₁₆	1.5	1.2	1.3
RuCl ₄	2.5	2.2	1.6

21. That the atomic percent of chlorine at the surface of the ruthenium oxide coating on the titanium foil was about 40% less for the ruthenium nitrosyl nitrate sprayed precursor in comparison to the ruthenium chloride precursor.

22. That the atomic percent of chlorine at a depth of about 20 Å into the thickness of the ruthenium oxide coating was about 46% less for the ruthenium nitrosyl nitrate sprayed precursor in comparison to the ruthenium chloride precursor.

23. That the atomic percent of chlorine at a depth of about 50 Å into the thickness of the ruthenium oxide coating was about 19% less for the ruthenium nitrosyl nitrate sprayed precursor in comparison to the ruthenium chloride precursor.

24. That the differences described in sections 24 to 26 above between the atomic percent of chlorine for the ruthenium oxide coating derived from the ruthenium nitrosyl nitrate sprayed precursor in comparison to the ruthenium chloride precursor are significant, in my opinion.

25. That, in my opinion, chlorine is an undesirable contaminant in a coating intended to be of ruthenium oxide. For example, when coupled with a tantalum anode, the thusly-manufactured pseudocapacitive component is useful as a cathode for an electrolytic capacitor. When chlorine is present, it leaches into the electrolyte and slowly attacks the tantalum oxide (TaO_5).

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26. That it is known by me, and generally understood by those skilled in the art of electrical energy storage devices, that chlorine contaminated tantalum oxide has a higher leakage current than tantalum oxide that is not so contaminated.

27. That higher leakage currents result in longer charge times, lower charge/discharge efficiency and possibly electrical failure or complete electrical breakdown, and for these reasons are undesirable, especially when the electrical energy storage device is a capacitor.

28. That none of the prior art patents cited against the presently pending claims teach, much less suggest, dissolving a ruthenium-containing precursor substantially devoid of a halide in a solvent that does not contain an alcohol or a halide and then ultrasonically spray depositing the solution on a heated substrate for the purpose of providing a pseudocapacitive component.

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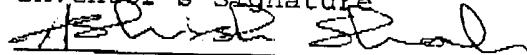
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29. As an inventor signing below:

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Inventor's Signature



Ashish Shah

Date: October 3, 2003